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# The Homogeneity Ranges of the $L1_2$ -Type Intermetallic Compounds $Ni_3Ga$ and $Ni_3Ge$

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**The homogeneity ranges of the  $L1_2$ -ordered compounds  $Ni_3Ga$  and  $Ni_3Ge$  and the boundaries of the neighboring phases have been examined by electron probe microanalysis using heterophase alloys in the temperature ranges 1073 to 1373 K (Ni-Ga) and 1073 to 1346 K (Ni-Ge). The composition ranges of the  $L1_2$ -ordered phases have been found to be narrower than those reported in the literature, on the Ga-rich side for  $Ni_3Ga$  and on the Ge-deficient side for  $Ni_3Ge$ .**

## 1. Introduction

The existence of the  $L1_2$ -ordered  $Ni_3Ga$  ( $\alpha'$ ) phase in the Ni-Ga system was first reported by [54Pea]. [57Pea] determined the phase boundaries around the  $\alpha'$  phase by measuring the variation of the lattice parameter with Ga concentration. [79Fes] reexamined the phase boundary compositions by electron probe microanalysis (EPMA). These data are used in the latest phase diagram of the Ni-Ga system [91Lee].

In the Ni-Ge system, the range of existence of the  $L1_2$ -ordered  $Ni_3Ge$  ( $\beta$ ) phase was first investigated by [40Rut] and reexamined by [80Day] by EPMA. According to the latter, the composition range of the  $\beta$  phase is from 22.5 to 25.0 at.% Ge over the temperature range 973 to 1273 K. These results are included in the assessed phase diagram of the Ni-Ge system [91Nas]. Recently, [95Kom] also reported the equilibrium compositions between  $\alpha$  and  $\beta$  phases using a diffusion couple composed of pure Ni and  $Ni_3Ge$ .

In a series of interdiffusion experiments on  $Ni_3Ga$  and  $Ni_3Ge$  by the present authors [98Ike, 98Non], precipitates of second phase were found after long-time annealing in some of the alloys that were supposed to be of  $L1_2$  single phase. The authors have thus reexamined the phase boundaries of  $Ni_3Ga$  and  $Ni_3Ge$ , as well as those of the neighboring intermetallic phases.

## 2. Experimental Procedure

Alloys of Ni-Ga and Ni-Ge were prepared by melting appropriate amounts of Ni of 99.97% purity, Ga of 99.9999% purity, and Ge of 99.9999% purity using an argon arc furnace. The compositions of the alloys are listed in Table 1. According to the phase diagram of the Ni-Ga system [91Lee], alloy 1a is in the heterophase region in equilibrium of  $\alpha$  (Ni solid solution) +  $\alpha'$  ( $Ni_3Ga$ ) phases, while alloy 1b is in the  $\alpha' + \beta$  ( $NiGa$ ) region above 1222 K, in the  $\alpha' + \gamma$  ( $Ni_3Ga_2$ ) region between 1014 and 1222 K, and in the  $\alpha' + \delta$  ( $Ni_5Ga_3$ ) region below 1014 K. Ni-Ge alloys 2a and 2c are in the  $\alpha$  (Ni solid solution) +  $\beta$  phase ( $Ni_3Ge$ ) region, while 2b is in the  $\delta$  ( $Ni_5Ge_2$ ) +  $\epsilon$  ( $Ni_5Ge_3$ ) region between 1318 and 1372 K, in the

$\beta + \epsilon$  between 779 and 1318 K and in the  $\beta + Ni_2Ge$  region below 779 K, according to the phase diagram of the Ni-Ge system [91Nas]. Alloy 2d was prepared to have bulk composition of 25.0 at.% Ge, but turned out to contain precipitates of the  $\delta$  phase in the matrix of the  $\beta$  phase in some parts. The  $\beta$  matrix in such parts must have more than 25.0% Ge as the local composition; such specimens were used to examine the equilibrium between the  $\beta$  and  $\delta$  phases at high temperatures, while the exact composition is not known. The volume fraction of the precipitates of the  $\delta$  phase was about 10%. Alloys 1a and 1b were unidirectionally solidified using an alumina crucible of 10 mm in diameter by the Bridgman method under a vacuum better than  $3 \times 10^{-3}$  Pa and were subjected to homogenization annealing at 1378 K for 24 h under a vacuum of  $1 \times 10^{-3}$  Pa. All alloys were cut into plates 2 mm thick. Each specimen thus prepared was wrapped with a Ta foil, sealed in a quartz capsule under a vacuum better

**Table 1** Compositions of alloys of Ni-X (X = Ga or Ge)

Alloy	Composition ( $c_X$ ), at. %
<b>Ni-Ga</b>	
1a	21.8
1b	31.5
<b>Ni-Ge</b>	
2a	18.0
2b	30.0
2c	23.2
2d	25.0(a)
(a) See text.	

**Table 2** Annealing conditions for Ni-Ga alloys

Specimen	Temperature, K	Time, h
1a-1	1373	168
1b-1	1373	228
1a-2	1273	597
1b-2	1273	597
1a-3	1183	615
1b-3	1183	615
1a-4	1073	1612
1b-4	1073	1612

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than  $1 \times 10^{-3}$  Pa and annealed under the conditions shown in Table 2 for Ni-Ga alloys and in Table 3 for Ni-Ge alloys. The temperature was measured with a Pt/Pt-13% Rh thermocouple and was held constant within  $\pm 1$  K. After annealing, the specimen was quenched by dropping the capsule into water.

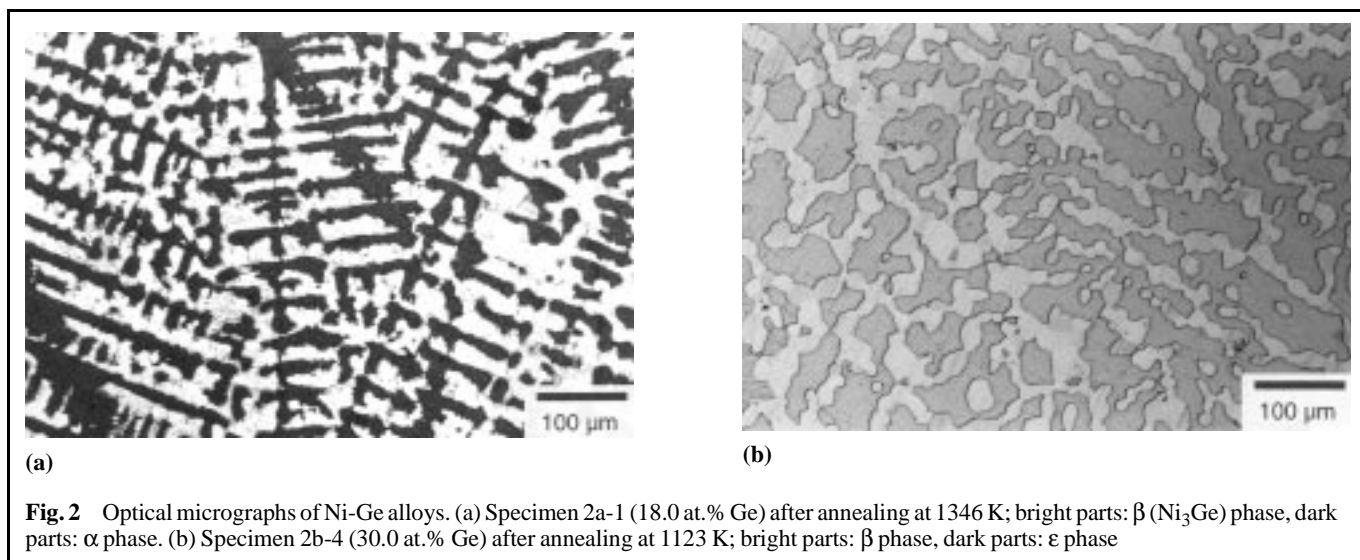
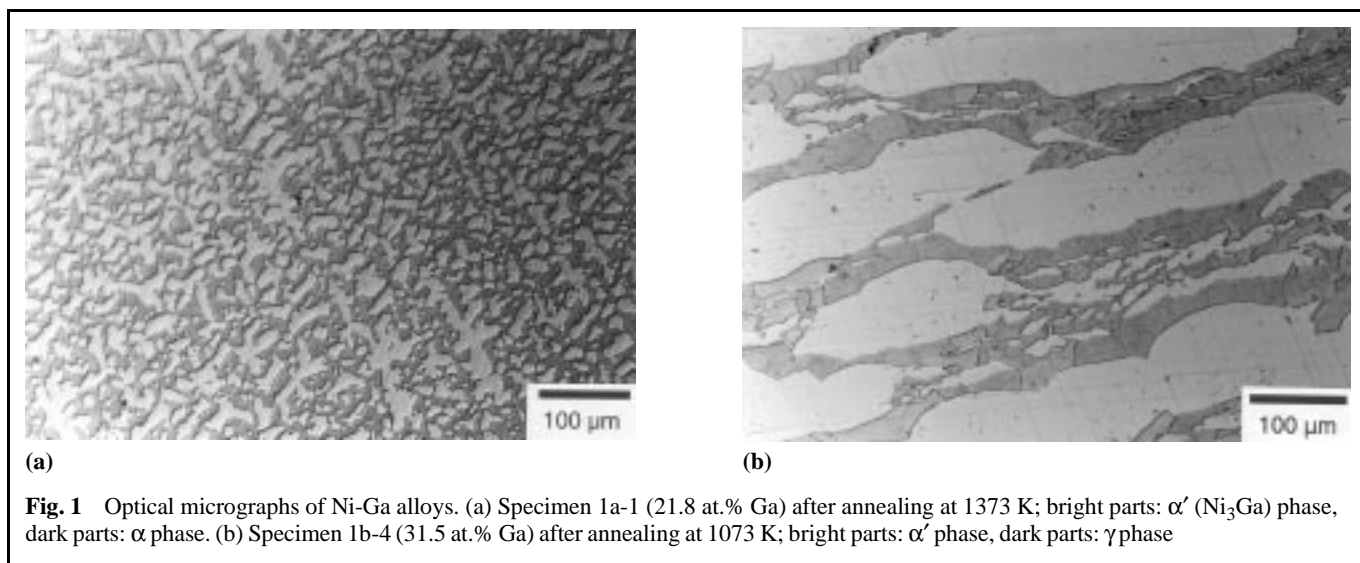
Metallographic examinations were made by optical microscopy after annealing. The surface was polished mechanically and etched using a solution of 20 g  $\text{Cu}_2\text{SO}_4 + 100 \text{ cm}^3 \text{HCl} + 100 \text{ cm}^3 \text{H}_2\text{O}$ .

The compositions of the constituent phases were determined by EPMA. The compositions of more than three points in each phase were measured using Shimadzu EPMA C1 model 40 with a wavelength-dispersive detector, which is equipped with a LiF crystal at a takeout angle of  $52.5^\circ$ . The accelerating voltage was 20 kV, and the nominal probe size was 1  $\mu\text{m}$ . The intensities of Ni  $K\alpha$  and Ga  $K\alpha$  or Ge  $K\alpha$  were measured from constituent phases and were converted to compositions by the ZAF method [94Fle]. (ZAF is an x-ray program that corrects for atomic number,  $Z$ , absorption,  $A$ , and fluores-

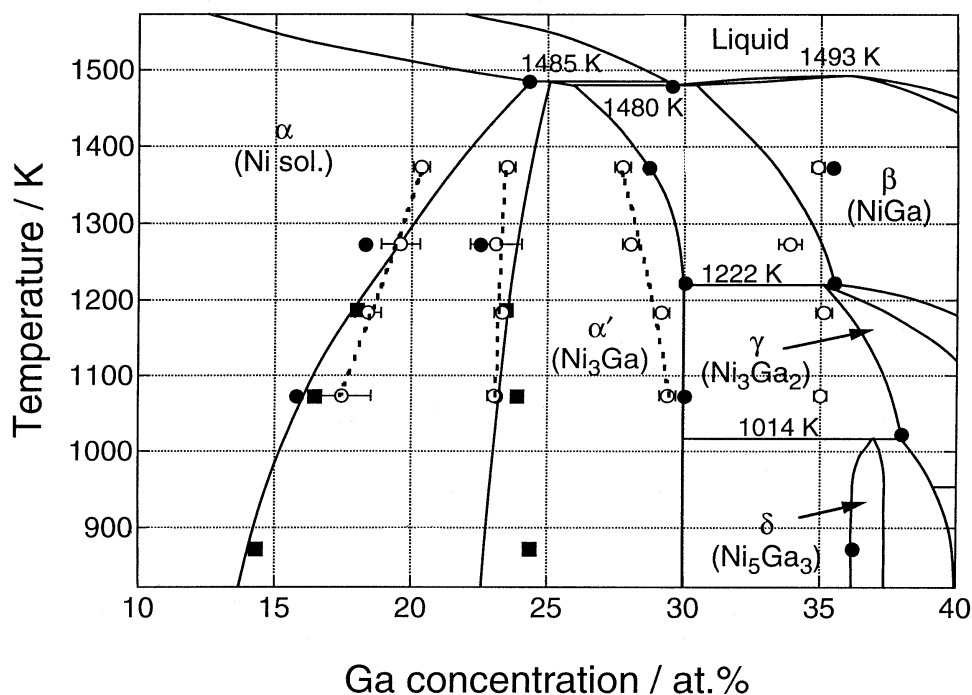
cence,  $F$ , effects in a matrix.) For Ni-Ga alloys, the standard intensities used for the conversion were obtained from a specimen of  $\alpha'$  single phase,  $\text{Ni}_{74.78}\text{Ga}_{25.22}$ , whose composition was

**Table 3** Annealing conditions for Ni-Ge alloys

Specimen	Temperature, K	Time, h
2a-1	1346	116
2b-1	1351	31
2d	1341	90
2a-2	1303	138
2b-2	1303	138
2a-3	1203	1054
2b-3	1203	1054
2a-4	1123	888
2c	1123	335
2b-4	1123	888
2a-5	1073	1224
2b-5	1073	1224



## Section I: Basic and Applied Research



**Fig. 3** Partial phase diagram of the Ni-Ga system. Open circle, this study; closed square, [57Pea]; closed circle, [79Fes]. Dashed lines: determined by this study. Solid lines: assessed by [91Lee]

**Table 4** Phase-boundary compositions of the phase equilibrium between  $\alpha$  (Ni solid solution) and  $\alpha'$  ( $\text{Ni}_3\text{Ga}$ ) phases and between  $\alpha'$  and  $\beta$  ( $\text{NiGa}$ ) or  $\gamma$  ( $\text{Ni}_3\text{Ga}_2$ ) phases in the Ni-Ga system

Temperature (T), K	Specimen	Composition ( $c_{\text{Ga}}$ ), at. %				
		$\alpha$ in ( $\alpha + \alpha'$ )	$\alpha'$ in ( $\alpha + \alpha'$ )	Specimen	$\alpha'$ in ( $\alpha' + \beta$ or $\gamma$ )	$\beta$ or $\gamma$ in ( $\alpha' + \beta$ or $\gamma$ )
1373	1a-1	20.36 $\pm$ 0.27	23.52 $\pm$ 0.27	1b-1	27.74 $\pm$ 0.28	34.87 $\pm$ 0.25 ( $\beta$ )
1273	1a-2	19.57 $\pm$ 0.73	23.12 $\pm$ 0.97	1b-2	28.11 $\pm$ 0.25	33.85 $\pm$ 0.42 ( $\beta$ )
1183	1a-3	18.39 $\pm$ 0.45	23.36 $\pm$ 0.27	1b-3	29.19 $\pm$ 0.28	35.12 $\pm$ 0.27 ( $\gamma$ )
1073	1a-4	17.42 $\pm$ 1.08	23.06 $\pm$ 0.25	1b-4	29.38 $\pm$ 0.27	35.01 $\pm$ 0.26 ( $\gamma$ )

determined by inductively coupled plasma spectrometry with an estimated error of  $\pm 0.24$  at.%. The standard intensities for Ni-Ge alloys were obtained from the  $\beta$  phase ( $\text{Ni}_3\text{Ge}$ ) formed in specimen 2b-2; its composition was found to be 25.0 at.% Ge by an analysis based on the standard intensities from the NiGe phase, which is a line compound at 50 at.% Ge [91Nas].

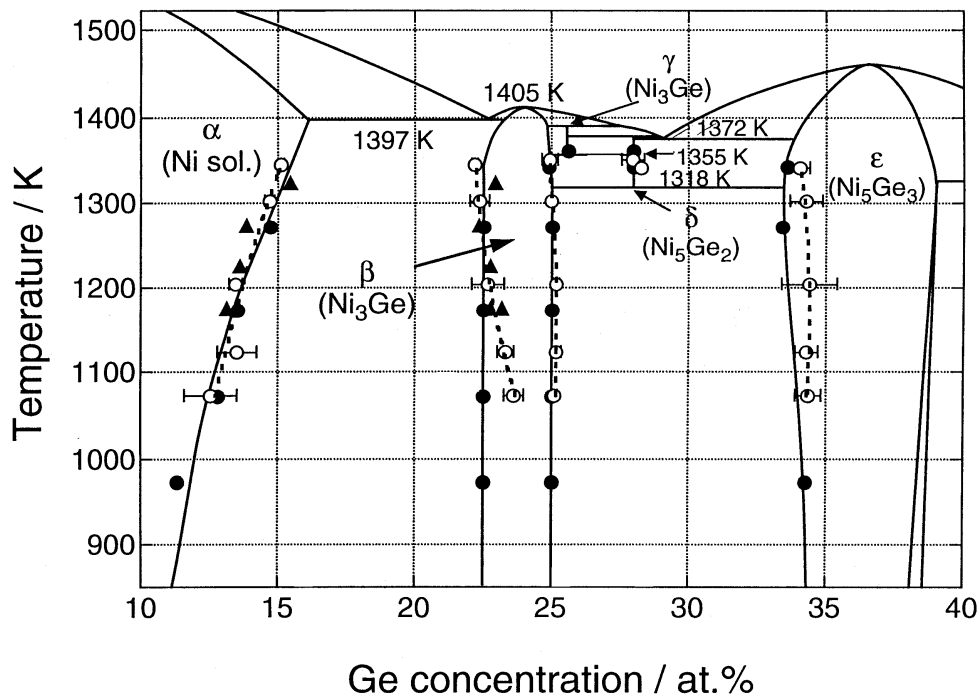
### 3. Results and Discussion

Figures 1 and 2 show optical micrographs of the Ni-Ga and Ni-Ge alloys, respectively. The dimensions of the microstructure, 5 to 50  $\mu\text{m}$ , are sufficiently large for EPMA with a probe size 1  $\mu\text{m}$ . The composition of each phase was determined by averaging 3 to 11 measurements. The results are summarized in Table 4 for Ni-Ga alloys and in Table 5 for Ni-Ge alloys. The concentrations in the tables are the average values of measured points. These results are shown as partial phase diagrams in Fig. 3 and 4. The composition of the  $\beta$  phase in the Ni-Ge system coexisting with the  $\alpha$  phase at 1123 K was not obtained since the microstructure of the  $\beta$  phase in speci-

men 2a-4 after annealing was not sufficiently large. The composition of the  $\beta$  phase was obtained from 2c.

Figure 3 shows the Ni-rich part of the phase diagram of the Ni-Ga system. The solubility of Ga in Ni and the boundary composition of the  $\alpha'$  phase on the Ga deficient side are in agreement with the previous reports. On the other hand, the boundary composition of the  $\alpha'$  phase on the Ga-rich side obtained by the present work is off from the line assessed by [91Lee] toward lower Ga concentrations by 1 or 2 at.%. The boundary composition of the  $\gamma$  phase coexisting with the  $\alpha'$  phase also deviates by 2 to 3 at.%. The assessment by [91Lee] is mostly based on the EPMA of two-phase alloys by [79Fes]. The discrepancies are probably due to much shorter annealing times (two orders of magnitude) employed by [79Fes]; their specimens might not be in complete equilibrium. The position of the  $\alpha' + \beta/\beta$  boundary obtained in the present work also deviates from that based on the work by [79Fes].

Figure 4 shows the Ni-rich part of the phase diagram of the Ni-Ge system assessed by [91Nas], together with the phase-



**Fig. 4** Partial phase diagram of the Ni-Ge system. Open circle, this study; closed circle, [80Day]; closed triangle, [95Kom]. Dashed lines: determined by this study. Solid lines: assessed by [91Nas]

**Table 5** Phase-boundary compositions of the phase equilibrium between  $\alpha$  (Ni solid solution) and  $\beta$  ( $\text{Ni}_3\text{Ge}$ ) phases and between  $\beta$  and  $\delta$  ( $\text{Ni}_5\text{Ge}_2$ ) or  $\epsilon$  ( $\text{Ni}_5\text{Ge}_3$ ) phases in the Ni-Ge system

Temperature (T), K	Specimen	Composition ( $c_{\text{Ge}}$ ), at. %				
		$\alpha$ in ( $\alpha + \beta$ )	$\beta$ in ( $\alpha + \beta$ )	Specimen	$\beta$ in ( $\beta + \delta$ or $\epsilon$ )	$\delta$ or $\epsilon$ in ( $\beta + \delta$ or $\epsilon$ )
1351	...	...	...	2b-1	$24.91 \pm 0.29$	$27.95 \pm 0.40$ ( $\delta$ )
1346	2a-1	$15.13 \pm 0.15$	$22.23 \pm 0.14$	...	...	...
1341	...	...	...	2d	...	$28.29 \pm 0.14$ ( $\delta$ )
						$34.03 \pm 0.34$ ( $\epsilon$ )
1303	2a-2	$14.68 \pm 0.17$	$22.37 \pm 0.36$	2b-2	Standard for the ZAF conversion	$34.27 \pm 0.61$ ( $\epsilon$ )
1203	2a-3	$13.46 \pm 0.25$	$22.69 \pm 0.62$	2b-3	$25.19 \pm 0.11$	$34.40 \pm 0.99$ ( $\epsilon$ )
1123	2a-4(a)	$13.49 \pm 0.71$	...	2b-4	$25.20 \pm 0.16$	$34.30 \pm 0.39$ ( $\epsilon$ )
	2c	...	$23.36 \pm 0.28$	...	...	...
1073	2a-5	$12.57 \pm 0.95$	$23.65 \pm 0.33$	2b-5	$25.15 \pm 0.14$	$34.36 \pm 0.47$ ( $\epsilon$ )

(a) See text.

boundary compositions determined in the present experiment. One important difference is the composition limit of the Ge-deficient side of the  $\beta$  phase. The present result shows reduction of the homogeneous range with decreasing temperature, while in the previous diagram based on the report by [80Day] is virtually temperature-independent. The experiment on Ni/ $\text{Ni}_3\text{Ge}$  couples by [95Kom] supports the trend observed in the present work.

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